NASA TECHNICAL TRANSLATION NASA TT F-13,888

FLAME-INHIBITING PVC MIXTURES WITH CHLOROPARAFFINS. Part 2

K. M. Bell, B. W. McAdam, H. J. Caesar

Translation of "Flammhemmende PVC-Mischungen mit Chlorparaffinen," Kunststoffe, Vol. 59, No. 6, 1969, pp. 344-346.

N72-14146 (NASA-TT-F-13888) FLAME-INHIBITING PVC MIXTURES WITH CHLOROPARAFFINS. PART 2: MIXTURES WITH PHTHALIC ACID ESTER-PRIMARY PLASTICIZERS K.M. Bell, et al (NASA) Nov. 1971 8 p CSCL 07D G3/06
Unclas
11735

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C. 20546
NOVEMBER 1971

FLAME-INHIBITING PVC MIXTURES WITH CHLOROPARAFFINS

Part 2. Mixtures with Phthalic Acid Ester-Primary Plasticizers*

K. M. Bell, B. W. McAdam, H. J. Caesar

Report made by the Technical Service Department,
Solvents and Monomers Group, Mond Division,
Imperial Chemical Industries Ltd., The Heath,
Runcorn, Cheshire, Great Britain.

ABSTRACT: PVC mixtures plasticized with DIOP or DIOP/chloroparaffins cannot be regarded as flame inhibiting. The flame inhibition quality is only considerably improved by an addition of 5 parts by weight of antimony oxide. The low temperature strength of the mixtures is better than those made using phosphoric acid esters or phosphoric acid esters/chloroparaffins. Sb_2O_3 is relatively expensive and an addition of 5 parts by weight appreciably increases the volume costs.

Tables 9 and 10 show for each plasticizer system the properties of the most promising PVC mixtures. Mixtures with phosphate plasticizers and an addition of 10 parts by weight of DIOP offer no advantages with respect to the plasticizer systems treated. They were therefore not included. For purposes of comparison, the properties of mixtures containing no chloroparaffins are also given.

In part 1 of this work, investigative findings were described concerning PVC plastic mixtures with primary plasticizers made from phosphoric acid esters and with chloroparaffins used as secondary plasticizers. Part 2 is concerned with parallel testing in which phthalic acid esters were used as primary plasticizers. The progressive exchange of DIOP by means of chloroparaffins up to the limit of tolerance succeeds in improving flame inhibition which, however, only appears sufficiently after addition of antimony oxide. In comparison to phosphate plasticizers and PVC mixtures containing chloroparaffins, such mixtures with comparable flame inhibition reveal better qualities at low temperatures, although having neither light transparency nor cost advantage. /344**

PVC plastic mixtures with Di-isooctyl-phthalate (DIOP) and chloroparaffins

DIOP is a flammable plasticizer and its addition to a PVC mixture causes a decrease in flame resistance. This behavior can be partially or wholly

* Synthetics (Kunststoffe) Vol. 59, No. 5, 1969, pp. 272-276. Tables and footnotes are numbered continuing from part 1.

** Numbers in the margin indicate pagination in the foreign text.

compensated for by the addition of antimony oxide or be reduced by means of the partial exchange of the DIOP with a nonflammable secondary plasticizer such as chloroparaffin. In order to confirm this, corresponding mixtures were prepared and examined (cf. Table 7).

Flame inhibition

PVC mixtures which contain DIOP burn differently than those having nonflammable plasticizers. The phthalate plasticizer tends to boil out in the proximity of a flame. Vaporizing DIOP can be ignited and the fine pointed flame appearing can occasionally further damage the test specimen. The results of the ignition test are quite varied, yet the statistical evaluation does show typical differences.

The flame inhibiting effect with PVC masses plasticized only with DIOP is poor. For a mixture of Shore A-hardness 80, combustible lengths of 145 mm were measured. Combustible lengths of more than 534 mm were also measured for a Shore A-hardness 64. Consistent with the ignitibility of DIOP, the ignitibility increases with rising plasticizer content. An addition of chloroparaffin improves the flame inhibition. However, even with the highest acceptable exchange quantity, it is less than in the case of the PVC mixtures with phosphate plasticizers and chloroparaffins described in part 1. The flame inhibiting effect of chloroparaffins grows with increasing chlorine content, and as in the case of the systems plasticized with phosphates, the ®Cereclor-Type with 52% chlorine content also leads here to better results.

When, in addition to chloroparaffin, 5 parts by weight (to 100 parts PVC) of antimony oxide are added to the mixture, it follows that a perceptible improvement in flame inhibition is achieved in both hardness areas. PVC mixtures which contain, in addition to DIOP, the highest possible proportion of chloroparaffin as well as additionally 5 parts of Sb_2O_3, can be characterized as good flame inhibiting (combustible length = 63.5 to 69 mm, compared with 38 to 63.5 mm in the case of the phosphate plasticizer/chloroparaffin without addition of Sb_2O_3). It is possible that the mixture with the phosphate plasticizer/chloroparaffin comes out better as far as flame inhibition is concerned using another method than the method (BS 2782-508 C) selected here.

Strength at low temperatures

The low temperature strength with mixtures plasticized with DIOP and chloroparaffins is considerably better than the comparable mixtures with phosphate plasticizers. The effect of a partial exchange of DIOP by chloroparaffins on the low temperature strength of a PVC mixture was the subject of earlier investigations[2]. If DIOP is exchanged in increasing quantity by chloroparaffin with 52% chlorine content so as to achieve mixtures of equal resilience, it follows that the low temperature strength is slightly decreased. In the case of the 42% chloroparaffin, no noteworthy change is to be determined whereas, in the case of the 45% chloroparaffin, a slight improvement appears. The results at hand confirm these observations although the data recorded in Table 7 should /345
be interpreted with care since not all mixtures show the same hardness.

Volume costs

In contrast to the more expensive phosphate plasticizers, the volume costs are less for DIOP. Although the savings which can be achieved by using chloroparaffins instead of DIOP are less than when phosphoric acid esters are used (cf. Table 1), they are important. On the other hand, when an addition of 5% of the relatively expensive antimony oxide is necessary in order to achieve a flame inhibiting effect, this in turn increases the volume costs of the mixture. As a matter of fact, the volume costs in Great Britain for PVC mixtures with DIOP/chloroparaffins/Sb_2O_3 are the same or occasionally a little higher than those mixtures using phosphate plasticizers/chloroparaffin.

TABLE 7. COMPOSITION AND PROPERTIES OF PVC PLASTICIZING MIXTURES USING DIOP AND DIOP/CHLOROPARAFFINS

Composition (with 100 parts by weight PVC)					Properties					Costs			
	Cereclor									England		Germany	
DIOP	42	S45	S52	Sb_2O_3	BS resilience	Shore-A-hardness	Combustible length (in)	Cold flex-Temperature [°C]	Cold bend-Temperature [°C]	Volume costs [d/0,1 gal]	Cost saving [%]	Volume costs [DM/l]	Cost saving [%]
47					34	80	5,7	—15	—30	17,70		1,446	
38	15				34	80	3,7	—16	—35	17,12	3,30	1,421	1,78
35	20				32	81	4,8	—17	—35	16,93	4,36	1,413	2,34
35		20			30	77	5,2	—21	—40	16,93	4,36	1,413	2,34
29		25			35	79	5,1	—18	—35	16,78	5,16	1,409	2,61
35			20		36	78	3,1	—16	—35	17,10	3,41	1,476	1,38
26			33		35	79	3,6	—20	—35	16,74	5,43	1,416	2,12
47				5	35	79	2,7	—18	—35	18,67		1,590	
38	15			5	35	79	2,7	—22	—35	18,25	3,26	1,560	1,87
35	20			5	37	78	2,5	—21	—35	18,06	4,30	1,551	2,47
35		20		5	46	76	2,5	—22	—40	18,06	4,30	1,551	2,47
29		25		5	37	78	2,5	—28	—40	17,93	4,97	1,549	2,59
35			20	5	34	80	2,4	—17	—35	18,23	3,37	1,566	1,52
26			33	5	34	80	2,5	—15	—30	17,87	5,31	1,544	2,27
74					70	58	>21	—46	—50	17,22		1,407	
60	22				60	64	12,2	—38	—45	16,55	3,89	1,379	2,01
65	15				55	67	11,2	—33	—50	16,75	2,72	1,387	1,43
50		22			67	60	13,3	—27	—40	16,65	3,29	1,389	1,28
50		32			62	63	10,0	—40	—50	16,29	5,42	1,390	2,66
60			22		65	61	5,8	—36	—50	16,70	3,04	1,391	1,45
50			32		64	62	7,2	—34	—45	16,50	4,17	1,388	1,38
74				5	70	58	2,5	—40	—45	18,18		1,525	
60	22			5	67	60	2,7	—38	—40	17,48	3,83	1,493	2,09
65	15			5	71	58	2,7	—39	—45	17,69	2,69	1,502	1,50
60		22		5	71	58	2,7	—41	—50	17,65	2,90	1,511	0,88
50		32		5	66	61	2,6	—41	—50	17,23	5,21	1,485	2,61
60			22	5	69	59	2,0	—32	—45	17,44	2,98	1,506	1,22
53			32	5	67	60	2,2	—32	—45	17,45	3,97	1,504	1,33

Commas represent decimal points.

TABLE 8. COMPOSITION AND PROPERTIES OF PVC PLASTICING MIXTURES WITH DIOP/TCP AND CHLOROPARAFFINS

Composition (with 100 parts by weight PVC)						Properties					Costs			
		Cereclor									England		Germany	
DIOP	TCP	42	S45	S52	Sb_2O_3	BS. resilience	Shore-A hardness	Combustible length (in)	Cold flex-Temperature [°C]	Cold bend-Temperature [°C]	Volume costs [d/0,1 gal]	cost saving [%]	Volume costs [DM/l]	Cost saving [%]
38	10					37	78	3,5	—15	—40	18,62		1,516	
30	10	15				38	77,5	2,8	—16	—35	17,98	3,42	1,486	1,95
25	10	20				34	80	3,0	—16	—40	17,83	4,24	1,481	2,30
25	10		20			39	77	3,1	—17	—40	17,84	4,23	1,481	2,30
18	10		28			37	78	2,6	—19	—30	17,56	5,66	1,472	2,95
15	10			35		36	78,5	2,2	—13	—30	17,57	5,62	1,482	2,24
25	10			20		35	79	2,4	—13	—30	18,00	3,28	1,496	1,32
38	10				5	37	78	2,5	—13	—25	19,78		1,660	
30	10	15			5	35	79	2,2	—15	—30	19,10	3,42	1,625	2,12
25	10	20			5	33	80,5	2,4	—14	—30	18,96	4,15	1,621	2,36
25	10		20		5	39	77	2,1	—18	—30	18,96	4,15	1,621	2,56
18	10		28		5	38	77,5	2,3	—17	—35	18,70	5,47	1,611	2,93
15	10			35	5	36	78,5	1,9	—12	—25	18,70	5,47	1,621	2,35
25	10			20	5	36	78,5	2,5	—11	—30	19,15	3,20	1,637	1,39
63	10					72	57,5	3,0	—28	—45	18,00		1,467	
51	10	20				71	58	3,2	—30	—40	17,35	3,64	1,438	1,98
57	10	15				76	55	2,7	—30	—45	17,46	3,02	1,441	1,79
51	10		20			73	57	3,0	—34	—50	17,35	3,64	1,438	1,98
42	10		38			77	54,5	2,5	—35	—50	16,78	6,82	1,411	3,80
51	10			20		71	58	2,0	—31	—45	17,40	2,85	1,450	1,17
35	10			41		67	60	2,5	—25	—40	17,02	5,44	1,437	2,03
63	10				5	76	55	2,0	—16	—40	18,97		1,586	
51	10	20			5	70	58,5	2,5	—27	—46	18,29	3,60	1,554	1,98
57	10	15			5	71	58	2,2	—31	—50	18,39	3,07	1,550	1,79
51	10		20		5	67	60	1,9	—33	—45	18,29	3,60	1,554	1,98
42	10		38		5	70	58,5	2,0	—36	—50	17,68	6,80	1,522	3,80
51	10			20	5	69	59	2,2	—30	—40	18,44	2,51	1,566	1,17
35	10			41	5	63	63	1,8	—27	—40	17,97	5,28	1,553	2,03

Commas represent decimal points.

TABLE 9. CONTRAST OF THE PROPERTIES OF PVC PLASTICIZING MIXTURES (SHORE A-HARDNESS ≈ 80; BSS 30 to 40)

	Costs		Composition (in parts by weight)											
	[d/lb.]	[DM/kg]	TCP			TXP			DIOP			DIOP/TCP		
PVC	12	1,00	100	100	100	100	100	100	100	100	100	100	100	100
TCP	24	1,90	40	15	7	—	—	—	—	—	—	10	10	10
TXP	19	2,10	—	—	—	40	15	7	—	—	—	—	—	—
DIOP	15,3	1,25	—	—	—	—	—	—	47	29	26	38	18	15
Cereclor S45	8,75	0,90	—	45	—	—	45	—	—	25	—	—	28	—
Cereclor S52	8,75	0,90	—	—	58	—	—	58	—	—	33	—	—	35
Sb_2O_3	32	3,80	—	—	—	—	—	—	5	5	5	—	—	—
Ba/Cd stabilizer	65	6,40	2	2	2	2	2	2	2	2	2	2	2	2
Epoxydized soy bean oil	45	2,00	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2	2	2
BS resilience			33	40	33	39	40	37	35	37	34	37	37	36
Shore-A-hardness			80,5	76	80,5	77	76	78	80	78	80	78	78	79
Combustion length in in.			2,1	2,6	2,5	2,2	2,3	2,6	2,7	2,5	2,5	3,5	2,6	2,2
Cold flex-Temperature [°C]			+ 1	—17	—10	+ 3	—15	— 9	—18	—22	—15	—15	—19	—13
Cold bend-Temperature [°C]			—20	—30	—25	—10	—35	—25	—35	—40	—30	—40	—30	—30
														79
Volume costs of the mixture [d/0,1 gal]			22,44	17,41	16,70	20,22	16,70	16,41	18,67	17,93	17,87	18,62	17,56	17,57
[DM/l]			1,892	1,505	1,457	1,808	1,482	1,446	1,590	1,549	1,544	1,516	1,472	1,482

Commas represent decimal points.

TABLE 10. CONTRAST OF THE PROPERTIES OF PVC PLASTICIZING MIXTURES (SHORE A-HARDNESS ≈ 60; BSS 60 to 80)

	Costs		Composition (in parts by weight)											
	[d/lb.]	[DM/kg]	TCP			TXP			DIOP			DIOP/TCP		
PVC	12	1,00	100	100	100	100	100	100	100	100	100	100	100	100
TCP	24	1,90	77	38	44	—	—	—	—	—	—	10	10	10
TXP	19	2,10	—	—	—	77	38	44	—	—	—	—	—	—
DIOP	15,3	1,72	—	—	—	—	—	—	74	50	53	63	42	35
Cereclor S45	8,25	0,90	—	50	—	—	50	—	—	32	—	—	38	—
Cereclor S52	8,75	0,90	—	—	57	—	—	57	—	—	32	—	—	41
Sb_2O_3	32	3,80	—	—	—	—	—	—	5	5	—	—	—	—
Ba/Cd stabilizer	65	6,40	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0	2,0
Epoxydized soy bean oil	45	2,00	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5	2,5
BS resilience			71	69	75	71	68	77	70	66	67	72	77	63
Shore-A-hardness			58	59	76	58	59,5	54,5	58,5	—	—	57,5	54,5	63
Combustion length in in.			1,6	1,7	1,7	1,6	1,7	1,7	2,5	2,6	2,2	3,0	2,5	1,8
Cold flex-Temperature [°C]			—16	—30	—21	—11	—28	—25	—40	—41	—32	—28	—35	—27
Cold bend-Temperature [°C]			—20	—35	—35	—20	—40	—25	—45	—50	—45	—45	—50	—40
Volume costs of the mixture [d/0,1 gal]			23,37	18,58	18,98	20,47	17,25	17,51	18,18	17,23	17,45	18,00	16,78	17,02
[DM/l]			1,876	1,564	1,600	1,876	1,364	1,600	1,525	1,485	1,504	1,467	1,411	1,437

Commas represent decimal points.

Phthalate-phosphate plasticizing mixtures in plasticized masses of PVC

PVC masses which have been plasticized with DIOP and DIOP/chloroparaffin show insufficient flame inhibiting properties unless antimony oxide is added. There is an alternative to the addition of Sb_2O_3 which consists in the supplying of small quantities of phosphate plasticizers which not only act as plasticizer but also improves the flame inhibiting property. Provided that the quantity of phosphoric acid ester can be kept small (not more than 10 parts to a 100 parts by weight of PVC), its negative effect on the strength at low temperature cannot be important.

Flame inhibition

Flame inhibition with PVC mixtures which have been plasticized by DIOP is considerably improved by the addition of 10 parts by weight of tricresyl-phosphate (TCP). In the case of the more plastic PVC mixtures, the combustible length is reduced from more than 534 mm to 76.5 mm and these mixtures can be regarded as flame inhibiting. Additions of chloroparaffin furnish a further improvement in both hardness regions. In this way, relatively inexpensive PVC mixtures with good flame inhibiting qualities as well as good strength at low temperatures can be obtained. As a matter of fact, a slight but significant further improvement in the flame inhibiting quality is obtained by the addition of 5 parts by weight of antimony oxide although this accordingly greatly increases the volume costs.

Low temperature strength

The addition to the mixture of only 10 parts by weight of TCP causes no essential change in the strength at low temperatures of the PVC mixture. The low temperature strength is accordingly relatively good, and especially in the case of mixtures containing the 45% type chloroparaffin.

Volume costs

The improvement of the flame inhibiting property of a PVC mixture plasticized with DIOP in the Shore A-hardness range 60 by addition of 10 parts by weight of TCP causes an increase in volume costs by 0.9 or .4%. In the Shore A-hardness 80 the costs for Great Britain of a PVC mixture plasticized with DIOP/TCP/chloroparaffin are approximately the same as for a PVC mixture plasticized with TCP/chloroparaffin, and in addition, the latter has better flame inhibiting qualities. (Chloroparaffins accommodate better with TCP than with DIOP, and consequently, greater quantities of TCP can be exchanged enabling higher percentage wise savings to be achieved). In Germany where different price relationships prevail, the PVC mixtures with DIOP/TCP/chloroparaffin are less expensive than those with TCP/chloroparaffin.